

EXHIBIT

A

Purification of Single-Shell Nanotubes**

By Erik Dujardin, Thomas W. Ebbesen,* Ajit Krishnan,
and Michael M. J. Treacy

The recent discoveries of methods^[1,2] for large-scale synthesis of single-shell nanotubes has opened the door to studying their physical and chemical properties, which are expected to be quite unique.^[3,4] However, the samples still contain large amounts of impurities (typically 30 % or more), such as amorphous carbon and catalytic metal particles, that need to be eliminated for accurate measurements, whether one studies the bulk or the individual tubes. Here we report an extremely simple and efficient method for removing most of the impurities from the nanotube samples.

It was believed that purification of single-shell nanotubes based on preferential oxidation and/or separation using surfactants was much more difficult than that of multishell nanotubes.^[5-8] For instance, gas-phase oxidation, which yields purified multishell nanotubes,^[5] destroys the single-shell nanotubes before anything else in the sample. So efforts have been directed at modifying other techniques originally developed for multishell nanotubes.^[9,10] Tohji et al.^[9] published a method using ultrasonication in water and treatment with hydrochloric acid. The yield of pure single-shell nanotubes is only 2 % of the starting material for a 48 h process. More recently, Bandow et al.^[10] reported a method mainly based on microfiltration under overpressure. A major advantage of this process is that it is driven by pure physicochemical interactions of the carbon products with the amphiphilic molecules and the filter membrane, leaving the nanotubes undamaged. The most serious drawback is the dependence of this procedure on the quality of the sample. It is known that sonicating nanotubes for a long period of time and at a high frequency can cause damage by breaking the nanotubes up into smaller pieces.^[11] We have found it hard to successfully apply this method to all samples. Typically, significant amounts of amorphous carbon and catalytic particles remain.

The one-step method presented here does not appear to be sensitive to the quality of the starting material. Moreover, it eliminates at the same time the carbonaceous material and most of the catalytic metal content.

The single-shell nanotubes were prepared by the laser-oven ablation method^[1] (see Experimental section). In this way, up to 30 mg/h of raw material could be synthesized, providing that the focused laser spot was continuously moved on the target surface to uniformly ablate the superficial material. Among all the parameters of this method, this one seems to be the most critical in order to obtain good yields. The transmission electron microscopy (TEM) pictures in Figure 1 show the quality of such raw single-shell nanotube samples. Typically, there is a mixture of ca. 50 % of bundles of single-shell nanotubes and ca. 50 % of carbonaceous material, gray graphitic nanoparticles, and black catalyst (cobalt and nickel) grains (Fig. 1a). A closer examination (Fig. 1b) of the tubes shows a layer of irregular thickness of amorphous carbon coating the bundles, which is particularly abundant where the bundles cross.

In the desire to open single-shell nanotubes with acids, we processed the raw nanotube samples in boiling concentrated nitric acid (See Experimental section). This method was developed for opening and filling multishell nanotubes by Green and co-workers.^[12] To our surprise, the nanotube sample seemed to become purer. After refluxing the sample for



Fig. 1. TEM micrographs at low (a, scale bar 0.2 μm) and high (b, scale bar 20 nm) magnification of as-synthesized single-shell nanotubes. Microscope Hitachi H9000-NAF, 100 kV.

[*] Prof. T. W. Ebbesen^[1]

ISIS, Louis Pasteur University
4 rue Blaise Pascal, F-67081 Strasbourg (France)

E. Dujardin

Laboratoire de Chimie des Interactions Moléculaires
Collège de France

31 place Marcelin Berthelot
F-75231 Paris Cedex 05 (France)

Dr. A. Krishnan, Dr. M. M. J. Treacy

NEC Research Institute

4 Independence Way, Princeton, NJ 08536 (USA)

[+] Present address: NEC Research Institute, 4 Independence Way, Princeton, NJ 08536, USA.

[**] The authors are grateful for the assistance of M. Büher and Nan Yao in the course of this work.



4 h in 70 % nitric acid at 120 °C, it was pure. The result of such a treatment is shown in Figures 2a and 2b. It is striking that the single-shell nanotubes appeared to be sufficiently (chemically) inert for a large proportion to survive such strongly oxidizing conditions. The yields, in terms of left-over weight of the sample after oxidation, can be as high as 50 %, which appears to reflect the initial nanotube content.

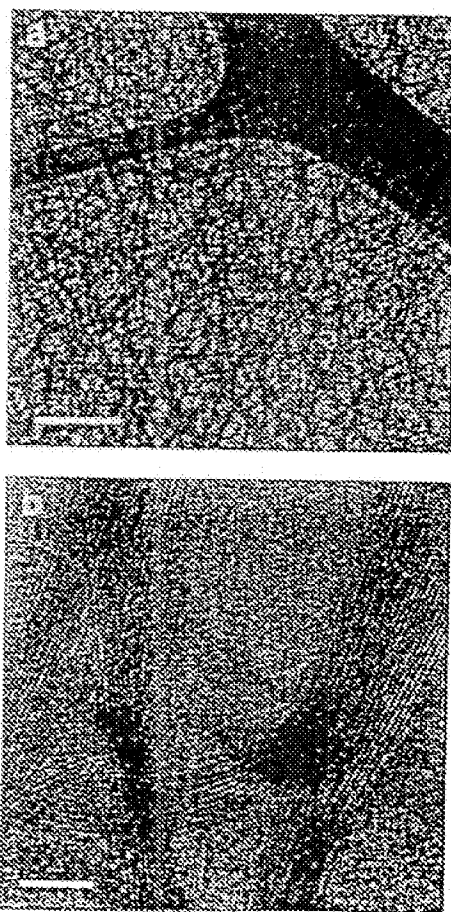


Fig. 2. TEM micrographs at low (a, scale bar 0.1 μm) and high (b, scale bar 20 nm) magnification of as-synthesized single-shell nanotubes purified by treatment in boiling nitric acid. Microscope Hitachi HX1000-NAR, 100 kV. Note: The treated samples are more sensitive to the TEM beam than the original material, probably due to the presence of the oxides.

Large areas of the mat formed by the pure single-shell nanotubes on the TEM grids revealed no severe damage to the walls of the nanotubes, as shown in Figure 2b. The nitric acid not only reacts preferentially with the particles but it leaves most of the tubes intact in the bundles. Occasionally one can see isolated tubes but it is very difficult to tell whether the tubes are open or not because of the low contrast of a single carbon wall. Some debris can still be seen on the outside of the bundles. Probably, after removing the impurities, the acid reacts with the outermost tubes of the bundles. In other words, the outer tubes in the bundle protect the inner ones.

In this regard, it should also be noted that no distortion or loss of contrast is visible in the TEM pictures of the walls

of the single-shell nanotubes in the purified samples. This could mean that the sp^2 structure is mostly conserved and that the amount of sp^3 carbons bearing alcohol, carboxylic or carbonyl functions is quite small. This is unlike multi-shell nanotubes, where these functional groups are found to cover the entire surface.^[6] Nevertheless, those hydrophilic groups are undoubtedly present on the purified single-shell nanotubes since the purified nanotubes are much more stable in aqueous suspensions than the raw ones. Like multishell tubes, annealing of the samples at high temperature should eliminate residual surface oxides.^[14]

Although we did not see any remaining catalytic particles in the sample, a chemical analysis was performed on the samples to quantify the amount of metal before and after purification. Interestingly, while the target contained 2 % metal (Ni and Co, total weight percent), the amount in the raw nanotube samples was 3 %. In terms of nanotube content this about 6 %, while purification leaves ca. 1 %. In other words, the metal content is reduced by a factor of six relative to the nanotube content. The 1 % is still surprisingly large considering that these metals readily dissolve in the acid. We are currently trying to find ways of removing the remaining metal.

A final remark is warranted. Due to their high curvature, nanotubes pick up impurities from just standing in air or in a solvent. This can be a very fast process, occurring in a day or even less, depending on the environment. It results in the nanotubes being coated with a sheath of amorphous material, which is easily observed by TEM. Needless to say this can have significant consequences on any property measurements.

It seems clear from this study that the kinetics of the reactivity of single-shell nanotubes is different from that of both multishell nanotubes and fullerenes. In particular they are relatively inert toward oxidation by acids, at least in a bundle form. This property allows the purification of the as-synthesized mixture by this fast, high-yield, and easy to handle procedure. This is by far the simplest and most reproducible method to date for both single and multishell tubes. It should be a helpful step for further physical or chemical experiments and technological applications.

Experimental

Purification Process: 10 mg of raw material (0.83 mmol of carbon) containing 40–60 % of single-shell nanotubes are sonicated in 5 mL of concentrated nitric acid (70 vol. %, 87.8 mmol) with a regular monofrequency ultrasonic bath (maximum power) for a few minutes. The suspension is then refluxed under magnetic stirring at 120–130 °C for 4 h. Dense yellow vapors of nitrogen dioxide evolve during the first 3 h, indicating a high rate of oxidation of hydrocarbons into alcohols, carboxylic acids, ketones, or aldehydes, and of metallic particles of cobalt and nickel into their corresponding ions. Later, the vapors become less dense as the nitric acid probably oxidizes less-reactive species.

The suspension is then cooled and centrifuged in glass tubes at 3400 rpm for 15 min, and the resulting yellow-brown solution is decanted. The wet powder is washed with portions of 10 mL of distilled water, centrifuged (3400 rpm, 15 min), and decanted iteratively as long as the solid settles down completely in 10 min (in general two or three washing cycles). The

pH of the successive washing solutions is monitored and is about six when the suspension of single-shell nanotubes starts to be stable on the centrifugation timescale. At this point, the powder is washed twice with 15 mL portions of nitric acid and filtered on fritted glass before rinsing twice with 15 mL portions of distilled water. Between each of these steps the suspension is sonicated. Finally, the wet powder is dried and kept in a desiccator under vacuum. The overall yield ranges between 30 and 50 %.

Synthesis of Single-Shell Nanotubes: A carbon target is made by mixing 31 g of graphite cement (Dylon Industries Inc.) with 2.78 g of graphite powder (GP-G, Dylon Industries Inc.), 0.35 g of cobalt (Aldrich, powder, $<2 \mu\text{m}$, 99.8 %), and 0.36 g of nickel (Aldrich, powder, submicrometer, 99.8 %). The homogeneous mixture containing 0.3 at.-% of each catalyst is melted in a 0.75 inch quartz tube (1 inch = 2.54 cm) and baked in air for 12 h at 120 °C and for 12 h at 200 °C. The baked target is then cured at 1350 °C for 5 h in vacuum (6×10^{-7} torr). For the nanotube synthesis, the target is placed in a 1 inch quartz tube under a pressure of 500 torr of argon and a gas flow of 400 cm³/min after several purges. The quartz tube is maintained at 1200 °C during the synthesis. A YAG-Nd laser (SED Titan-P, 10 Hz, 230 mJ/pulse at 532 nm, 270 mJ/pulse at 1064 nm) was used to generate pulsed beams at 1064 and 532 nm. The former is delayed by 13 ns with respect to the latter. Both beams are focused to a 3–4 mm spot on the target. For optimal yield, the focal spot of the beams is moved on the target every few minutes. After the synthesis runs, the quartz tube is cooled down to room temperature under argon flow. A fine web-like deposit then collects on the walls of the quartz tube and on the cold finger that closes this tube.

Received: December 5, 1997

Final version: April 16, 1998

- [1] T. Guo, P. Nikolaev, A. Thess, D. T. Colbert, R. E. Smalley, *Chem. Phys. Lett.* 1995, 243, 49; A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomasek, J. E. Fisher, R. E. Smalley, *Nature* 1996, 377, 483.
- [2] C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Deniard, R. Lee, J. E. Fischer, *Nature* 1997, 388, 756.
- [3] S. J. Tian, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs, C. Dekker, *Nature* 1997, 386, 474.
- [4] P. M. Ajayan, T. W. Ebbesen, *Rep. Prog. Phys.* 1997, 60, 1025.
- [5] T. W. Ebbesen, P. M. Ajayan, H. Hiura, K. Tanigaki, *Nature* 1994, 367, 519.
- [6] H. Hiura, T. W. Ebbesen, K. Tanigaki, *Adv. Mater.* 1995, 7, 275.
- [7] S. C. Tang, Y. K. Chen, P. J. F. Harris, M. L. H. Green, *Nature* 1994, 372, 159.
- [8] J.-M. Bonard, T. Stockli, J.-P. Salvetat, F. Maer, T. Stockli, C. Emschl, L. Forró, W. A. de Heer, A. Châtelain, *Adv. Mater.* 1997, 9, 327.
- [9] K. Tobe, T. Goto, H. Takahashi, Y. Shimoda, N. Shimizu, B. Jayadevan, I. Matsuoka, Y. Saito, A. Kasuya, T. Ohsuna, K. Hiraga, Y. Nishina, *J. Phys. Chem.* 1996, 100, 1974.
- [10] S. Bandow, A. M. Rao, K. A. Williams, A. Thess, R. E. Smalley, P. C. Eklund, *J. Phys. Chem. B* 1997, 101, 8839.
- [11] K. L. Lo, R. M. Lago, Y. K. Chen, M. L. H. Green, P. J. F. Harris, S. C. Tang, *Carbon* 1996, 34, 814.
- [12] M. Kosaka, T. W. Ebbesen, H. Hiura, K. Tanigaki, *Chem. Phys. Lett.* 1995, 233, 47.